



Short Note

Dichlorido(η^6 -*p*-cymene)[tris(2-cyanoethyl)phosphine]ruthenium(II)

William Henderson ^{1,*}, Ashwin Gopalan Nair ¹, Nathan R. Halcovich ² and Edward R. T. Tiekink ^{3,*}

¹ Chemistry, School of Science, University of Waikato, Private Bag 3105, Hamilton 3240, New Zealand; ashnair117@gmail.com

² Department of Chemistry, Lancaster University, Lancaster LA1 4YB, UK; n.r.halcovitch@lancaster.ac.uk

³ Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, No. 5 Jalan Universiti, Bandar Sunway 47500, Selangor Darul Ehsan, Malaysia

* Correspondence: bill.henderson@waikato.ac.nz (W.H.); edwardt@sunway.edu.my (E.R.T.T.); Tel.: +64-7-838-4656 (W.H.); +60-3-7491-7181 (E.R.T.T.)

Received: 15 September 2018; Accepted: 10 October 2018; Published: 12 October 2018

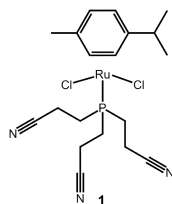


Abstract: The tris(2-cyanoethyl)phosphine (tcep) complex $[\text{RuCl}_2\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3\}(\eta^6\text{-}p\text{-cymene})]$ (*p*-cymene = *p*-CH₃C₆H₄ⁱPr) was synthesised by the bridge-splitting reaction of the chlorido-dimer $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$ with tcep. The complex was characterised by a single-crystal X-ray structure determination as well as NMR spectroscopy, ESI mass spectrometry, and microelemental analysis. X-ray crystallography shows the ruthenium atom is coordinated by *p*-cymene in a η^6 -fashion, two chlorides and the phosphorus atom of the tcep ligand with the donor set defining a distorted octahedral geometry. The ESI mass spectrometry study reveals that the complex readily forms negative ions $[\text{M} + \text{Cl}]^-$ and $[2\text{M} + \text{Cl}]^-$ by association with a chloride ion.

Keywords: ruthenium; tris(2-cyanoethyl)phosphine; *p*-cymene; ESI mass spectrometry; X-ray crystallography

1. Introduction

Tris(2-cyanoethyl)phosphine, $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ (tcep), is an interesting ligand on account of its simple synthesis [1] from commercially available $[\text{P}(\text{CH}_2\text{OH})_4]\text{Cl}$ and acrylonitrile, and its user-friendly properties; it is, unlike the majority of tertiary alkylphosphines, crystalline and air-stable. Its stereoelectronic properties have also attracted interest on account of its relatively small cone angle, that is, 132° [2,3]. Not surprisingly, there have been a number of studies on the coordination chemistry of this ligand [4], particularly towards transition metal centres, such as palladium and platinum [5–7] and gold [8]. However, relatively few ruthenium complexes of this ligand have been investigated to date [9–13]. The only examples of ruthenium π -hydrocarbon derivatives include the complexes $[\text{Ru}(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Cl}(\text{tcep})_2]$ ($\text{R} = \text{H}, \text{CH}_3, \text{CH}_3\text{CO}$) formed by reaction of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Cl}(\text{PPh}_3)_2]$ with excess tcep in toluene [14]. In recognition of the above, herein the synthesis, spectroscopic characterisation and X-ray crystal structure determination of the title complex, **1**, Scheme 1, are described.



Scheme 1. Chemical structure diagram for **1**.

2. Results and Discussion

Reaction of the *p*-cymene ruthenium chloride dimer $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$ (*p*-cymene = *p*- $\text{CH}_3\text{C}_6\text{H}_4^i\text{Pr}$) with $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ in refluxing ethanol results in the deposition of a salmon-red product $[\text{RuCl}_2\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3\}(\eta^6\text{-}p\text{-cymene})]$, which is poorly soluble in the reaction mixture. The product was readily isolated by filtration of the cooled reaction mixture, followed by washing and drying. The complex was also prepared using propan-1-ol in place of ethanol as the reaction solvent. The complex shows relatively low solubility in common organic solvents such as chloroform and methanol, but is soluble in DMF, DMSO, acetonitrile, and pyridine. Needle-like crystals of the ruthenium complex were obtained by vapour diffusion of diethyl ether and petroleum spirits into an acetonitrile solution, at room temperature. As there are no X-ray crystal structures of ruthenium tcp complexes reported in the literature, the structure of the title complex, **1**, was determined.

The molecular structure of **1** was determined by X-ray crystallography and is shown in Figure 1; selected geometric parameters are included in the caption of the figure. The ruthenium atom is coordinated by two chloride ligands, the phosphorus atom of tcp and *p*-cymene, which coordinates in an η^6 -mode. By convention, the latter ligand is defined to occupy three coordination sites so that the coordination geometry of the ruthenium atom may be considered distorted octahedral. The Ru–C(*p*-cymene) bond lengths span a relatively narrow range, that is, Ru–C15 = 2.1831(18) to Ru–C13 = 2.2374(18) Å, indicating a relative symmetric disposition of the ring with respect to ruthenium; the Ru \cdots ring centroid distance is 1.7009(8) Å. The Ru–Cl1 bond length is slightly longer than that of Ru–Cl2, which is correlated with the different intermolecular interactions involving these atoms, that is, as discussed below, the Cl1 atom forms more intermolecular contacts than does the Cl2 atom. The conformation adopted by the tcp molecule in its metal complexes has attracted some interest [5]. In **1**, consistent with expectation in the sterically unencumbered complex, the Ru–P1–C1–C2 [61.05(15)°], Ru–P1–C4–C5 [175.48(12)°], and Ru–P1–C7–C8 [−54.51(16)°] torsion angles indicate + syn-clinal, + anti-periplanar, and − syn-clinal conformations, respectively. Further, the P1–C1–C2–C3 [−176.59(14)°], P1–C4–C5–C6 [179.33(13)°], and P1–C7–C8–C9 [−69.3(2)°] torsion angles adopt the expected pattern of − anti-periplanar, + anti-periplanar, and − syn-clinal, respectively.

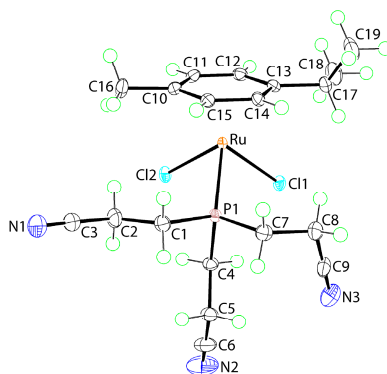


Figure 1. The molecular structure of **1** showing atom labelling and displacement ellipsoids at the 70% probability level. Selected geometric parameters: Ru–Cl1 = 2.4226(4), Ru–Cl2 = 2.4094(4), Ru–P1 = 2.3481(5), Ru–C15 = 2.1831(18), Ru–C13 = 2.2374(18) Å, Cl1–Ru–Cl2 = 89.990(15), Cl1–Ru–P1 = 84.343(16), Cl2–Ru–P1 = 84.672(16)°.

The molecular packing in the crystal of **1** (Figure 2) is dominated by weak, non-covalent C–H···Cl and C–H···N interactions; geometric details characterising these are given in Table 1. The presence of methylene- and phenyl-C–H···Cl contacts leads to supramolecular chains along the *b*-axis direction and with a helical topology. The chains are linked into a supramolecular layer parallel to (−1 0 1) via methylene- and phenyl-C–H···N(cyano) interactions. Of these, the interactions methylene-C–H···N1(cyano) occur between centrosymmetrically-related ethylcyano groups and lead to 16-membered {···HC₂PC₃N}_n synthons. The most notable contacts between layers are weak methyl-C–H···N(cyano) contacts that lead to helical {···HCCN}_n chains along the *b*-axis.

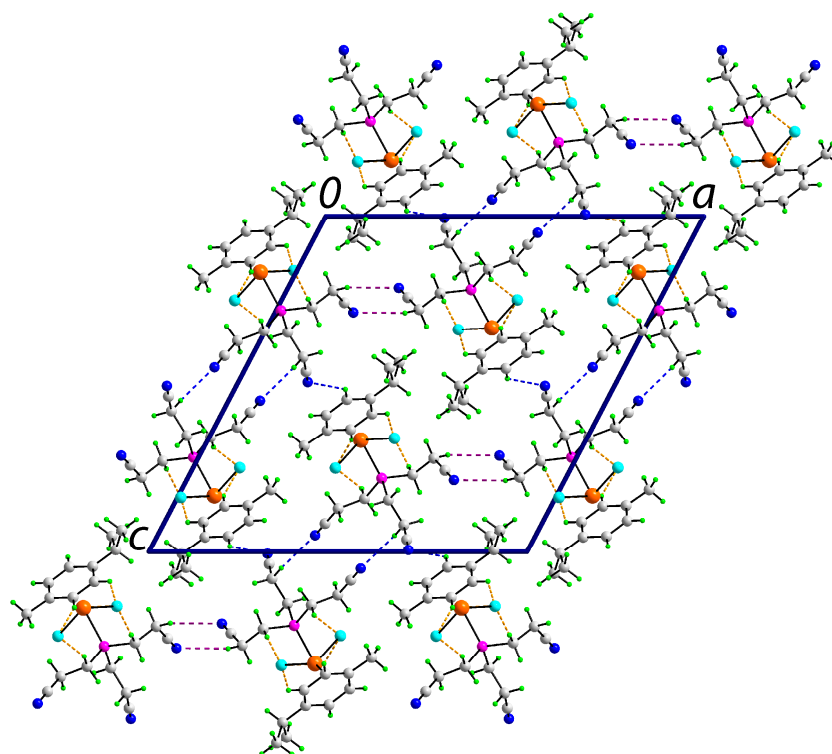


Figure 2. The molecular packing in the crystal of **1**: a view of the unit cell contents shown in projection down the *b*-axis. The intra-layer C–H···Cl and C–H···N contacts are indicated by orange and blue dashed lines, respectively, whereas the inter-layer C–H···N contacts are shown as purple dashed lines.

Table 1. Geometric parameters (Å, °) characterising the non-covalent (A–H···B) interactions present in the crystal of **1**.

A	H	B	A–H	H···B	A···B	A–H···B	Symmetry Operation
C1	H1b	Cl2	0.99	2.80	3.738(2)	158	$x, 1 + y, z$
C7	H7a	Cl1	0.99	2.73	3.711(2)	170	$x, 1 + y, z$
C14	H14	Cl1	0.95	2.80	3.446(2)	126	$x, 1 + y, z$
C15	H15	Cl1	0.95	2.83	3.461(2)	125	$x, 1 + y, z$
C15	H15	Cl2	0.95	2.68	3.5752(19)	157	$x, 1 + y, z$
C5	H5b	N1	0.99	2.51	3.402(3)	150	$1 - x, 2 - y, -z$
C12	H12	N2	0.95	2.57	3.289(3)	132	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$
C19	H19c	N3	0.98	2.69	3.636(3)	126	$\frac{1}{2} + x, 1\frac{1}{2} - y, \frac{1}{2} + z$

The ¹H and ¹³C{¹H} NMR spectra of **1** show the expected features; see Supplementary Materials for original spectra. In the ¹H NMR spectrum, the *p*-cymene ligand shows a distinctive multiplet at δ 2.61, a doublet at δ 1.19 from the isopropyl group, a CH₃ singlet at δ 1.98, and an AB pattern around δ 5.8 for the *para*-substituted aromatic ring. The CH₂ protons of the tcep ligand appear as two multiplets at δ 2.75 and 2.45. In the ¹³C{¹H} NMR spectrum, the cyano carbon appears as a distinctive doublet

resonance at δ 120.20, showing 3J coupling to phosphorus of 14.8 Hz. Assignment of the tcep CH_2 carbons as the doublet at δ 20.31 and singlet at δ 11.61 was facilitated by a DEPT135 NMR spectrum, which identified these resonances as CH_2 groups. The CH and CH_3 carbons of the *p*-cymene isopropyl group appear at δ 30.33 and 21.82, respectively, while the $\text{CH}_3\text{C}_6\text{H}_4$ methyl group appears at δ 17.48. These chemical shifts are comparable to other *p*-cymene ruthenium complexes, for example, δ 31.60, 22.30, and 19.03, respectively, in the complex $[\text{RuCl}(\text{NCCH}_3)_2](\eta^6\text{-}p\text{-cymene})\text{PF}_6$ [15]. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the complex in d_6 -DMSO showed a single resonance at δ 23.0. The complex was also characterised using ESI mass spectrometry; the complex was dissolved in a small quantity of a solvent (DMSO or pyridine) in which it is soluble, and then diluted with methanol. In positive-ion mode, the expected ion $[\text{RuCl}\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3\}(\eta^6\text{-}p\text{-cymene})]^+$ (m/z 464.16, calculated m/z 464.06) was observed in the DMSO-methanol solution. However, the spectra were relatively complex, and a number of ions were unable to be assigned. The use of pyridine as an ionisation aid, which has been successfully applied to a wide range of neutral metal-halide coordination complexes [16], failed to furnish the expected solvated ion $[\text{RuCl}\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3\}(\eta^6\text{-}p\text{-cymene})(\text{pyridine})]^+$. Accordingly, negative-ion mode was explored, and surprisingly, resulted in straightforward spectra, showing $[\text{RuCl}_2\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3\}(\eta^6\text{-}p\text{-cymene}) + \text{Cl}]^-$ (m/z 535.89, calculated m/z 536.00) as the base peak, together with $[2\{\text{RuCl}_2\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3\}(\eta^6\text{-}p\text{-cymene})\} + \text{Cl}]^-$ (m/z 1034.79, calculated m/z 1035.02). Given that the ruthenium centre is coordinately saturated, the most likely point of interaction of a chloride ion with the complex is via an interaction with the CH_2 protons of the tcep ligand. Such interactions between chloride ions and alkyl nitriles RCN ($\text{R} = \text{e.g., CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7$) are known, and are moderately strong (e.g., 63.4 kJ mol^{-1} for the interaction between Cl^- and propionitrile) [17]. Consistent with this, the negative-ion ESI mass spectrum of the free tcep ligand $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ in methanol, with added KCl, shows $[\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3 + \text{Cl}]^-$ as the base peak at m/z 228, together with $[2\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3\} + \text{Cl}]^-$ at m/z 421, while the analogous triphenylphosphane complex $[\text{RuCl}_2(\text{PPh}_3)(\eta^6\text{-}p\text{-cymene})]$ showed no ion $[\text{RuCl}_2(\text{PPh}_3)(\eta^6\text{-}p\text{-cymene}) + \text{Cl}]^-$ (expected m/z 536). The supramolecular interactions between CH_2 protons of the tcep ligand and the (coordinated) chloride ligands of $[\text{RuCl}_2\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3\}(\eta^6\text{-}p\text{-cymene})]$, as described in this work, also lend support to this proposal. The negative-ion mass spectrum of $[\text{RuCl}_2\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3\}(\eta^6\text{-}p\text{-cymene})]$ also showed a low intensity ion at m/z 497.92, assigned as $[\text{RuCl}_2\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3\}(\eta^6\text{-}p\text{-cymene})\text{-H}]^-$ (calculated m/z 498.02), presumably formed by deprotonation of a tcep ligand.

In conclusion, interesting negative ions $[\text{M} + \text{Cl}]^-$ and $[2\text{M} + \text{Cl}]^-$ ions, formed by association between the complex and chloride ion, are observed in the ESI mass spectrum. Crystallography reveals an octahedral structure consistent with literature expectation.

3. Materials and Methods

3.1. General Information

The starting complex $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$ was prepared by the literature procedure [15]. The ligand tris(2-cyanoethyl)phosphine (tcep) [1] was prepared according to the literature procedure, and was recrystallised from hot ethanol prior to use. Solvents used were at least of laboratory reagent grade, and were used as supplied from commercial sources: propan-1-ol, acetonitrile, diethyl ether (Ajax Finechem, Auckland, New Zealand); DMF, chloroform, petroleum spirits (Merck, Darmstadt, Germany); methanol, DMSO (Scharlau Chemie SA, Barcelona, Spain); and pyridine (BDH, Poole, England). Ethanol was a bulk Merck (Darmstadt, Germany) grade solvent, used as supplied.

ESI mass spectra were recorded on a Bruker MicrOTOF instrument (Bremen, Germany). A range of ionisation conditions were typically used, with the capillary exit voltage varying between 60 and 180 V, and the skimmer 1 voltage having one-third of the capillary exit voltage value. Ions were assigned by comparison of experimental and calculated isotope patterns; the latter were obtained using either proprietary instrument software, or mMass [18]. Elemental analyses were obtained from the Campbell

Microanalytical Laboratory, University of Otago, New Zealand. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker AVIII-400 instrument (Billerica, MA, USA), in d_6 -DMSO solution.

3.2. Synthesis of $[\text{RuCl}_2\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3\}(\eta^6\text{-}p\text{-cymene})]$

A mixture of $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$ (274 mg, 0.447 mmol) and two mole equivalents of $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ (172.8 mg, 0.895 mmol) in 100% ethanol (40 mL) was refluxed for 3 h, whereupon the initial orange-brown solution changed to a pink-red suspension after ca. 30 min. After standing at room temperature for 18 h, the precipitate was filtered, washed with cold methanol (2×10 mL) and petroleum spirits (2×20 mL), and dried under vacuum to give the product (353.1 mg, 79%). Found: C 45.68; H 5.39; N 8.33. $\text{C}_{19}\text{H}_{26}\text{Cl}_2\text{N}_3\text{PRu}$ requires C 45.70; H 5.25; N 8.41%. ^1H NMR, δ 5.82 [AB doublet, C_6H_4 , $J(\text{HH}) = 6.2$ Hz], 5.79 [AB doublet, C_6H_4 , $J(\text{HH}) = 5.7$ Hz], 2.75 [m, CH_2 of tcep, $J(\text{HH}) = 7.8$ Hz], 2.61 [m, CHMe_2 , $J(\text{HH}) = 6.9$ Hz], 2.45 [m, CH_2 of tcep, $J(\text{HH}) = 9.5$ Hz], 1.98 (s, Me), 1.19 [d, CHMe_2 , $J(\text{HH}) = 6.9$ Hz]. $^{13}\text{C}\{^1\text{H}\}$ NMR, δ 120.20 (d, CN, $J(\text{PC}) = 14.8$ Hz), 107.68 (s, C of C_6H_4), 96.03 (s, C of C_6H_4), 88.67 (s, C of C_6H_4), 88.63 (s, C of C_6H_4), 84.99 (s, C of C_6H_4), 84.93 (s, C of C_6H_4), 30.33 (s, CHMe_2), 21.82 (s, CHMe_2), 20.31 (d, PCH_2 , $J(\text{PC}) = 25.2$ Hz), 17.48 (s, MeC_6H_4), 11.61 (s, CH_2CN). $^{31}\text{P}\{^1\text{H}\}$ NMR (d_6 -DMSO), δ 22.9 (s). The complex is insoluble in dichloromethane, chloroform, and alcohols, but is soluble in acetonitrile, DMSO, and DMF.

The complex was also prepared as above from $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2]_2$ (400 mg) with tcep (260 mg) in hot propan-1-ol, giving $[\text{RuCl}_2\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3\}(\eta^6\text{-}p\text{-cymene})]$ in 71% yield.

3.3. Crystallography

Crystals of $[\text{RuCl}_2\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3\}(\eta^6\text{-}p\text{-cymene})]$ were obtained by diffusion of diethyl ether and petroleum spirits (b.p. 40–60 °C) into an acetonitrile solution of the complex at room temperature, giving deep red-orange needles. Intensity data for **1** were measured at $T = 100(2)$ K on a SuperNova Dual AtlasS2 diffractometer fitted with Mo $\text{K}\alpha$ radiation so that θ_{max} was 29.7°. Data reduction, including absorption correction, was accomplished with CrysAlis Pro [19]. Of the 12,741 reflections measured, 5104 were unique ($R_{\text{int}} = 0.022$), and of these, 4633 data satisfied the $I \geq 2\sigma(I)$ criterion. The structure was solved by direct methods [20] and refined (anisotropic displacement parameters and C-bound H atoms in the riding model approximation) on F^2 [21]. A weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (0.025P)^2 + 2.001P]$ was introduced, where $P = (F_o^2 + 2F_c^2)/3$. Based on the refinement of 225 parameters, the final values of R and wR (all data) were 0.024 and 0.057, respectively. The molecular structure diagram was generated with ORTEP for Windows [22] and the packing diagram using DIAMOND [23].

Crystal data for $\text{C}_{19}\text{H}_{26}\text{Cl}_2\text{N}_3\text{PRu}$ (**1**): $M = 499.37$, monoclinic, $P2_1/n$, $a = 19.4829(10)$, $b = 6.3232(2)$, $c = 19.5898(10)$ Å, $\beta = 117.723(6)^\circ$, $V = 2136.3(2)$ Å³, $Z = 4$, $D_x = 1.553$ g cm^{−3}, $F(000) = 1016$ and $\mu = 1.067$ mm^{−1}. CCDC (Cambridge Crystallographic Data Centre) deposition number: 1863516.

Supplementary Materials: The following are available online: $^{31}\text{P}\{^1\text{H}\}$ NMR, ESI mass spectra, and crystallographic data for **1** in crystallographic information file (CIF) format. CCDC 1857673 also contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>.

Author Contributions: Synthesis and spectroscopic characterisation was carried out by A.G.N. and W.H. X-ray crystallography was carried out by N.R.H. and E.R.T.T. The manuscript was written by E.R.T.T. and W.H.

Funding: This research received no external funding. The APC was funded by Sunway University.

Acknowledgments: The University of Waikato and Sunway University are thanked for financial support of this work, and Pat Gread is thanked for mass spectrometry assistance. WH thanks Albright & Wilson Ltd. (now Rhodia Consumer Specialities) for a generous gift of $[\text{P}(\text{CH}_2\text{OH})_4]\text{Cl}$, and Courtney Fox for preparing a sample of the complex for NMR characterisation.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Vullo, W.J. Hydroxymethyl replacement reactions of tetrakis(hydroxymethyl)phosphonium chloride. *Ind. Eng. Chem. Prod. Res. Dev.* **1966**, *5*, 346–349. [[CrossRef](#)]
2. Cooney, K.D.; Cundari, T.R.; Hoffman, N.W.; Pittard, K.A.; Temple, M.D.; Zhao, Y. A priori assessment of the stereoelectronic profile of phosphines and phosphites. *J. Am. Chem. Soc.* **2003**, *125*, 4318–4324. [[CrossRef](#)] [[PubMed](#)]
3. Brown, T.L.; Lee, K.J. Ligand steric properties. *Coord. Chem. Rev.* **1993**, *128*, 89–116. [[CrossRef](#)]
4. Fisher, K.J.; Henderson, W.; Dance, I.G.; Willett, G.D. Investigation of the properties of tris(2-cyanoethyl)phosphine by electrospray and Fourier transform ion cyclotron resonance mass spectrometries. *J. Chem. Soc. Dalton Trans.* **1996**, 4109–4113. [[CrossRef](#)]
5. Orpen, A.G.; Pringle, P.G.; Smith, M.B.; Worboys, K. Synthesis and properties of new tris(cyanoethyl)phosphine complexes of platinum(0,II), palladium(0,II), iridium(I) and rhodium(I). Conformational analysis of tris(cyanoethyl)phosphine ligands. *J. Organomet. Chem.* **1998**, *550*, 255–266. [[CrossRef](#)]
6. Costa, E.; Pringle, P.G.; Smith, M.B.; Worboys, K. Self-replication of tris(cyanoethyl)phosphine catalyzed by platinum group metal complexes. *J. Chem. Soc. Dalton Trans.* **1997**, 4277–4282. [[CrossRef](#)]
7. Lawrence, S.E.; Kelly, M.; Ni Dhubbghaill, O.M. Dichloro-trans-bis[tris(2-cyanoethyl)phosphine] palladium(II). *Acta Crystallogr. E* **2001**, *57*, m272–m273. [[CrossRef](#)]
8. Hussain, M.S.; Al-Arfaj, A.R.; Akhtar, M.N.; Isab, A.A. $[(\text{CEP})_2\text{Au}]\{[\text{Au}(\text{CN})_2]^-$: A compound with gold-gold bonds. *Polyhedron* **1996**, *15*, 2781–2785. [[CrossRef](#)]
9. Pruchnik, F.P.; Smolenski, P.; Raksa, I. Carbonyl rhodium(I) and ruthenium(II) complexes with water soluble phosphines. *Pol. J. Chem.* **1995**, *69*, 5–8.
10. Ballester-Reventos, L.; Gutierrez-Alonso, A.; Perpiñan-Vielba, M.F. Formation of heterobimetallic ruthenium-mercury nitrosyl complexes. *Polyhedron* **1991**, *10*, 1013–1017. [[CrossRef](#)]
11. Chen, L.; Poë, A.J. Systematic substituent effects on dissociative substitution kinetics of ruthenium carbonyl, $\text{Ru}(\text{CO})_4\text{L}$, complexes (L = phosphorus, arsenic, and antimony donor ligands). *Inorg. Chem.* **1989**, *28*, 3641–3647. [[CrossRef](#)]
12. Bruce, M.I.; Matison, J.G.; Nicholson, B.K. Cluster chemistry. XVII. Radical ion-initiated syntheses of ruthenium cluster carbonyls containing tertiary phosphines, phosphites, arsines, SbPh_3 or isocyanides. *J. Organomet. Chem.* **1983**, *247*, 321–343. [[CrossRef](#)]
13. Gutierrez-Alonso, A.; Ballester-Reventos, L. Reactions of carbonyl and nitrosyl ruthenium complexes with uninegative (X,S)-donor ligands (X = sulfur, phosphorus). *Polyhedron* **1991**, *10*, 1019–1023. [[CrossRef](#)]
14. Gutiérrez Alonso, A.; Ballester Reventós, L. Cyclopentadienylruthenium complexes with sulfur donor ligands. II. A comparative study of the reactivity of $\text{Ru}(\eta\text{-RC}_5\text{H}_4)\text{Cl}(\text{L})_2$ (R = H, CH_3 , CH_3CO ; L = CO, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2/2$, $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$) towards anionic (S-S) donor ligands. *J. Organomet. Chem.* **1988**, *338*, 249–254. [[CrossRef](#)]
15. Jensen, S.B.; Rodger, S.J.; Spicer, M.D. Facile preparation of η^6 -p-cymene ruthenium diphosphine complexes. Crystal structure of $[(\eta^6\text{-p-cymene})\text{Ru}(\text{dppf})\text{Cl}]\text{PF}_6$. *J. Organomet. Chem.* **1998**, *556*, 151–158. [[CrossRef](#)]
16. Henderson, W.; Evans, C. Electrospray mass spectrometric analysis of transition-metal halide complexes. *Inorg. Chim. Acta* **1999**, *294*, 183–192. [[CrossRef](#)]
17. Fridgen, T.D.; Burkell, J.L.; Wilsily, A.N.; Braun, V.; Wasylycia, J.; McMahon, T.B. Potential energy surfaces for gas-phase $\text{S}_{\text{N}}2$ reactions involving nitriles and substituted nitriles. *J. Phys. Chem. A* **2005**, *109*, 7519–7526. [[CrossRef](#)] [[PubMed](#)]
18. Strohm, M.; Hassman, M.; Košata, B.; Kodíček, M. mMass data miner: An open source alternative for mass spectrometric data analysis. *Rapid Commun. Mass Spectrom.* **2008**, *22*, 905–908. [[CrossRef](#)] [[PubMed](#)]
19. Rigaku Oxford Diffraction. *CrysAlis PRO*; Agilent Technologies Inc.: Santa Clara, CA, USA, 2015.
20. Sheldrick, G.M. A short history of SHELX. *Acta Crystallogr. A* **2008**, *64*, 112–122. [[CrossRef](#)] [[PubMed](#)]
21. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Crystallogr. C* **2015**, *71*, 3–8. [[CrossRef](#)] [[PubMed](#)]

22. Farrugia, L.J. WinGX and ORTEP for Windows: An update. *J. Appl. Crystallogr.* **2012**, *45*, 849–854. [[CrossRef](#)]
23. Brandenburg, K.; Putz, H. *DIAMOND*; Crystal Impact GbR: Bonn, Germany, 2006.

Sample Availability: A sample of the complex is not available from the authors.



© 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).